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A STUDY OF THE DECOMPOSITION OF LANNATE (METHOMYL) ON LETTUCE IN IMPERIAL COUNTY, CALIFORNIA FEBRUARY 1975

By

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INTRODUCTION

Methomyl is a toxic carbamate insecticide-nematocide with an acute oral LD_{50} (rats) of 17 mg/kg. Methomyl has been determined to be a toxicity category I pesticide based upon the oral and inhalation toxicity. The dermal LD_{50} in rabbits has been determined to be greater than 5,000 mg/kg. Poisoning is related to blood and tissue cholinesterase inhibition.

Methomyl provides broad spectrum control of many insects on many vegetables, fruit crops, field crops and ornamentals. More than 206,056 pounds of methomyl were applied to more than 348,000 acres of lettuce fields in 1975.

Methomyl is marketed as Lannate and Nudrin, a 90 percent water-soluble powder and a liquid containing 1.8 pounds of methomyl per gallon. This study was conducted on Lannate L; its label recommends for use on lettuce, 1-2 pints per acre with a seven-day preharvest interval and 2-4 pints per acre with a ten-day preharvest interval. The label states that workers should not be allowed to re-enter the treated field for 24 hours following application.

APPLICATION AND SAMPLING

Lannate L was applied to two lettuce fields (with phosdrin) in the following manner:

Field 1: 65 acres
3 pints Lannate (.675 lbs actual methomyl)/acre
1.9 pints Phosdrin/acre
15 gallons water/acre

Field 2: 48 acres
2.0 pints Lannate (0.45 lbs actual methomyl)/acre
1.5 pints Phosdrin/acre
15 gallons water/acre

Samples were collected in triplicate at intervals beginning with one hour after application. The studies were run for six days in Field 1 and four

days in Field 2. Each sample consisted of approximately 100 leaf punches, 2.5 cm in diameter. One sample was analyzed for total residue while the other two samples were run for penetrated and surface analysis.

ANALYTICAL METHODS (Extraction)

The procedure used for the extraction of dislodgeable, penetrated, and total residues from leaf punches was originally published by Guther in "The Bulletin of Environmental Contamination and Toxicology", 9, 243-249, 1973. It has been documented several times in detail, with modifications that were made to accommodate the various pesticides and their metabolites.

The sample container and leaf punches are weighed and the gross weight recorded.

Total Residues

1. The leaf punches are transferred to a blending jar. The empty sample container is again weighed and the net weight of the punches recorded.

2. Approximately 50 gms of sodium sulfate and 100 mls of ethyl acetate are added.

3. The sample is blended at high speed for three minutes, keeping the blender cup cool by immersing it in a container of cool water. The blender cup is removed and the sample allowed to settle.

4. An aliquot is decanted into a teflon-capped bottle and stored in the freezer prior to clean up and analysis.

Dislodgeable Residues

1. Fifty mls of water and approximately four drops of Sur-Ten solution (1:50) are added to the sample containers. The containers are capped and placed in a multi-purpose rotator and rotated at 30 cycles/min. for 60 minutes. The aqueous solution is decanted through a glass wool plug into a 500 ml separatory funnel.

2. The punches are rotated a second time, using 50 mls of water and four drops of Sur-Ten solution, for 30 minutes. This is added to the first extraction.

3. The sample is then hand-shaken for approximately 10 seconds with 30 mls of water. The container is drained into the separatory funnel with the first two extractions.

4. The aqueous solution is acidified with 1-N H_2SO_4, and extracted three times with 50 ml of ethyl acetate. The ethyl acetate is filtered through sodium sulfate into a glass stoppered mixing cylinder. An aliquot is decanted into a teflon-capped bottle and stored in the freezer prior to clean up and analysis.

Penetrated Residue

1. After the last water rinse is drained for the dislodgeable residue, the punches are transferred to a blender jar. The empty sample container is weighed and the net weight of the punches recorded.

2. Approximately 50 gms of sodium sulfate and 100 mls of ethyl acetate are added.

3. The sample is blended and handled the same as the total residue sample.

ANALYTICAL METHODS (Clean up and hydrolysis)

The sample was brought to room temperature and a 50 ml aliquot was added to 50 ml of water in a 125 ml 24/40 S.T. erlenmeyer flask. The flask was fitted with a triple ball Snyder column, placed on a hot plate, and heated until the ethyl acetate had evaporated.

Dislodgeable Residues

The cooled aqueous solution is acidified with 1-N H_2SO_4 and transferred to a 125 ml separatory funnel with water washes. The flask is rinsed with 50 ml of chloroform which is used to extract the aqueous solution. The aqueous solution is extracted a total of three times with 50 ml of chloroform for each extraction.

Total and Penetrated Residues

The cooled aqueous solution is acidified with 1-N H_2SO_4 and transferred to a 125 ml separatory funnel with water washes. The flask is rinsed with 30 ml of hexane which is used to extract the aqueous solution. The hexane layer is discarded and the aqueous solution was extracted three times with 50 ml of chloroform for each extraction.

Dislodgeable, Penetrated and Total Residues

The combined chloroform extracts are added to 50 ml of 0.1-N NaOH in a 250 ml 24/40 S.T. erlenmeyer flask. The flask is fitted with a triple ball Snyder column placed on a hot plate and heated until the chloroform had evaporated. The sample is heated an additional 15 minutes to insure complete hydrolysis.

The sample is cooled, acidified with 1-N H_2SO_4 transferred to 125 ml separatory funnels with water washes and extracted three times with 30 ml of ethyl acetate. The ethyl acetate extracts are filtered through sodium sulfate into a 125 ml 24/40 S.T. erlenmeyer flask. A 0.1 ml portion of triethylamine is added, the flask is fitted with a Snyder column, placed on a hot plate and carefully evaporated to approximately 5 mls. The sample is cooled and quantitatively transferred, to a 15 ml conical tube, to a volume of 10 mls.

Fifty microgram quantities of standard are periodically subjected to the clean-up and hydrolysis and used to quantitate the samples.

ANALYTICAL METHODS (Chromatography)

The samples are analyzed by gas chromatography using a Tracor model 550 equipped with a flame photometric detector in its sulfur mode and the following conditions:

Column - 3% FFAP, 100/120 Chrom W (HP); 6' x 1/4" x 2 mm I.D.

Column temp.	- 160°C	Flow rates	N_2	- 80 ml/min
Injector temp.	- 220°C		H_2	- 100 ml/min
Detector temp.	- 220°C		Air	- 80 ml/min
Retention time	- 1.8 min			

RESULTS

Weather conditions are recorded on Table 1. The average maximum and minimum temperatures were 77.7 and 33.8°F, respectively.

Results of the residue analysis are recorded on Tables 3 and 4 and on Figures 1 and 2. On Field 2, where the application rate was lower, the Lannate residues were approximately the same in 2-1/2 days as they were in 5 days on Field 2.

TABLE 1: DAILY TEMPERATURE AND PRECIPITATION
Weather Observations Taken at El Centro, California

Date (1975)	Temperature (°F) Maximum	Minimum	Precipitation (inches)
February 19	76	29	
20	76	30	
21	76	30	
22	74	30	
23	74	30	
24	78	35	
25	81	40	
26	82	40	
27	82	40	
Average	77.7	33.8	Total 0.00

TABLE 2: LANNATE RESIDUE ON LETTUCE IN FIELD 1

Sample Number	Date (1975)	Sample Interval	Surface Residue (ppm)	Penetrated Residue (ppm)	Total Residue (ppm)
66	2-19	1 hour	30.6	31.5	
67	2-19	1 hour	24.9	27.6	
68	2-19	1 hour			81.1
69	2-19	3 hours	38.5	20.4	
70	2-19	3 hours	28.5	24.2	
71	2-19	3 hours			51.7
72	2-19	5 hours	31.5	20.7	
73	2-19	5 hours	29.8	19.6	
74	2-19	5 hours			72.5
75	2-20	22 hours	24.2	17.3	
76	2-20	22 hours	20.9	17.9	
77	2-20	22 hours			63.9
78	2-21	46 hours	11.2	15.0	
79	2-21	46 hours	10.9	19.2	
80	2-21	46 hours			44.3
81	2-22	3 days	10.9	6.1	
82	2-22	3 days	9.3	7.4	
83	2-22	3 days			22.5
84	2-23	4 days	8.6	7.4	
85	2-23	4 days	12.3	8.8	
86	2-23	4 days			19.9
87	2-24	5 days	3.4	4.8	
88	2-24	5 days	3.8	3.7	
89	2-24	5 days			7.8

TABLE 3: LANNATE RESIDUES ON LETTUCE IN FIELD 2

Sample Number	Date (1975)	Sample Interval	Surface Residue (ppm)	Penetrated Residue (ppm)	Total Residue (ppm)
100	2-24	1 hour	24.9	19.5	
101	2-24	1 hour	18.5	13.3	
102	2-24	1 hour			54.5
103	2-25	13 hours	17.3	4.6	
104	2-25	13 hours	14.2	3.4	
105	2-25	13 hours			28.8
106	2-26	38 hours	6.4	4.9	
107	2-26	38 hours	6.5	5.9	
108	2-26	38 hours			16.3
109	2-27	62 hours	2.6	2.5	
110	2-27	62 hours	3.3	4.7	
111	2-27	62 hours			11.3

FIGURE 1: LANNATE RESIDUES ON HEAD LETTUCE IN FIELD 1
IMPERIAL COUNTY, CALIFORNIA FEBRUARY 1975

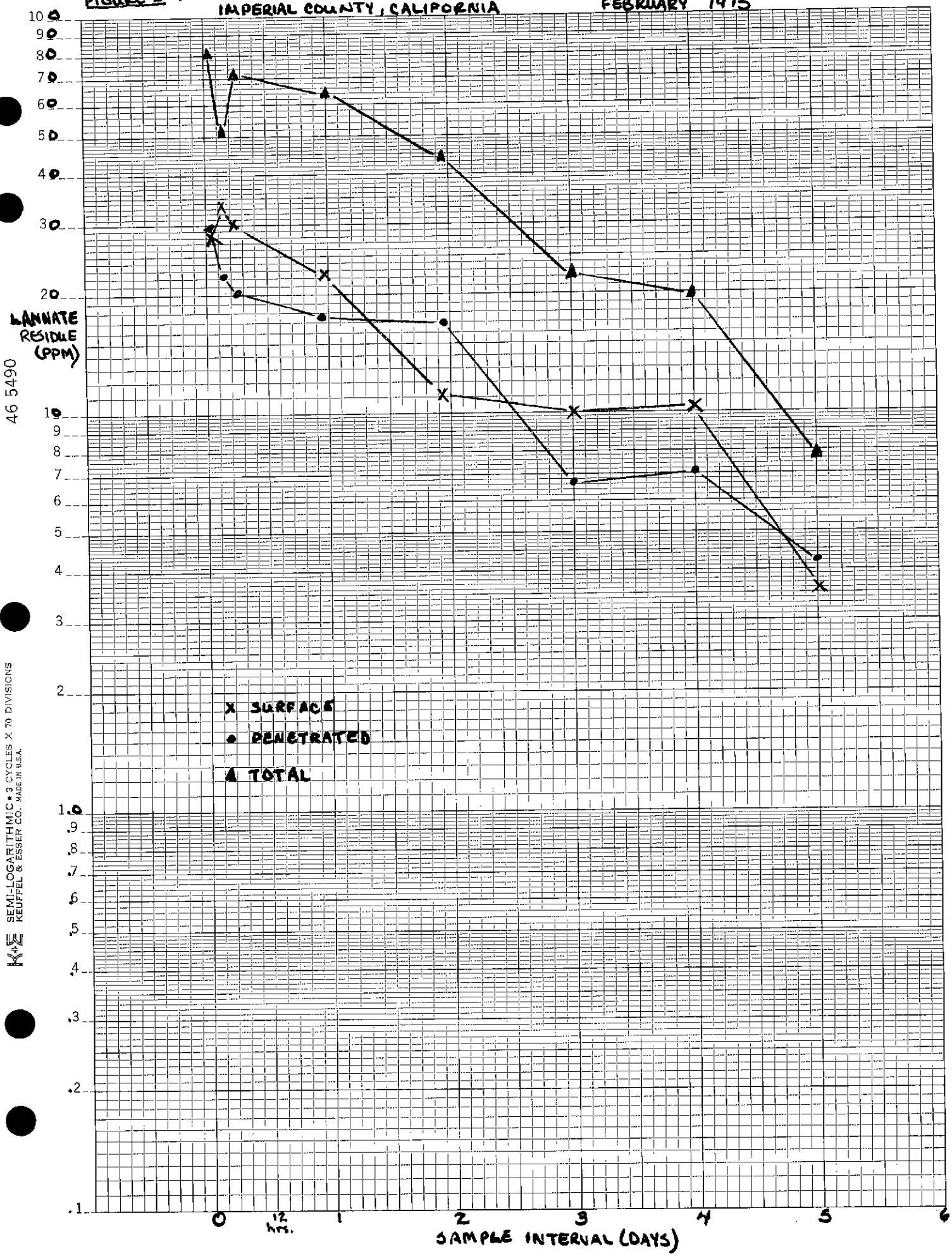

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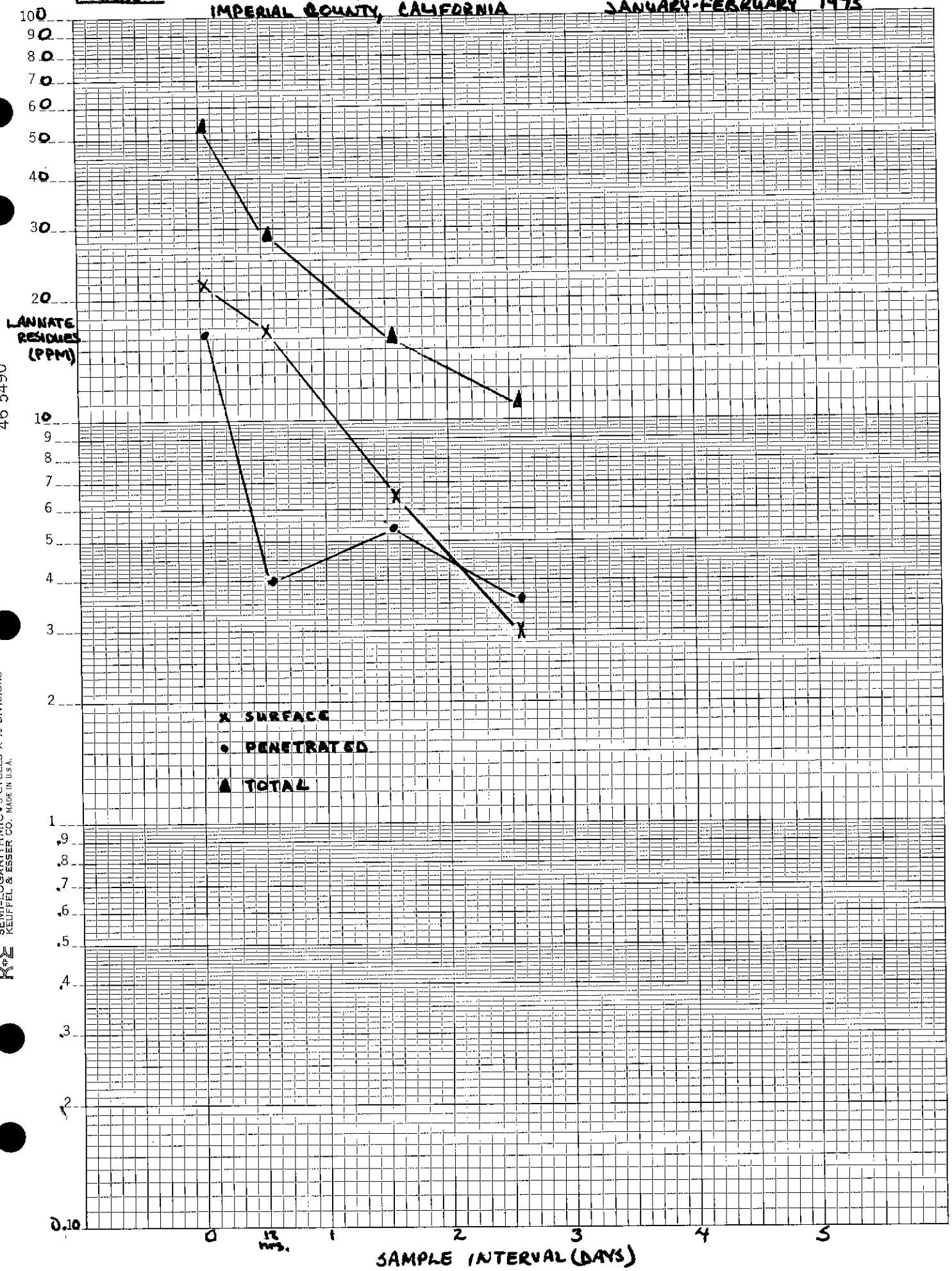
FIGURE 2: LANNATE RESIDUES ON HEADLETTUCE IN FIELD 2
IMPERIAL COUNTY, CALIFORNIA JANUARY-FEBRUARY 1975



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